

Sustained ferromagnetism induced by H-vacancies in graphane

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The electronic and magnetic properties of graphane with H-vacancies were investigated using the quantum-chemistry methods. The hybridization of the edges is found to be absolutely crucial in defining the size of the bandgap, which is increased from 3.04 eV to 7.51 eV when the hybridization is changed from the sp^2 to the sp^3 type. The H-vacancy defects also influence the size of the gap that depends on the number of defects and their distribution between the two sides of the graphane plane. Further, the H-vacancy defects induced on one side of the graphane plane and placed on the neighboring carbon atoms are found to be the source of ferromagnetism which is distinguished by the high stability of the state with a large spin number in comparison to that of the singlet state and is expected to persist even at room temperatures. However, the ferromagnetic ordering of the spins is obtained to be limited by the concentration of H-vacancy defects and ordering would be preserved if number of defects do not exceed eight.

INTRODUCTION

Graphene is the carbon-based wonder material which has gained wide attention due to its many unique electronic and magnetic properties. Despite the high mobility of the charge carriers in graphene resulting from its zero effective mass [1–3], the absence of gap hinders its application in nanoelectronics. The magnetic properties of graphene arising from spin ordering of the localized states at the zigzag edges [4] or by the presence of defects [6–10] might facilitate its application in carbon-based spintronics. If the localized states occupy the same sublattice then they can induce the sublattice imbalance and according to Lieb’s theorem [5] that can lead to the ground state being ferromagnetic [6, 7]. The room-temperature ferromagnetism in graphene has been obtained experimentally [11]. However, there are some issues involved in maintaining the ferromagnetic state whose stability depends on the concentration of the localized states, distance between states and size of the graphene flakes through the size of the band gap [6–10]. Therefore, disappearance of the gap in bulk graphene brings some inconsistencies in applying Lieb’s theorem [8].

Recently discovered graphane [15–18] – hydrogenated graphene – has brought new impetus in the investigation of carbon-based materials due to the predicted advantages in its application in nanoelectronics and spintronics. Termination of the carbon atoms by hydrogens leads to the generation of sp^3 carbon network removing the π bands from its band structure thereby generating a gap. It was theoretically predicted that fully hydrogenated graphane is non-magnetic and a wide band gap semiconductor [15, 19]. However, H-vacancy defects in graphane generate localized states characterized by non-zero magnetic moments (each defect has $\mu = 1.0\mu_B$ [20], where μ_B is the Bohr magneton [Fig.]). As graphane is characterized by a wide gap and the value of the charge transfer integral ($t_\sigma \sim 7.7$ eV [14]) is higher than that in graphene ($t_\pi \sim 2.4$ eV [14]), according to the Hub-

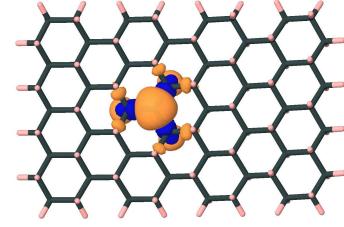


FIG. 1: The spin density for a single H-vacancy defect in graphane plotted with isovalues of ± 0.001 e/ \AA^3 .

bard model [6, 7] these should stabilize ferromagnetism in graphane (for example through an increase of the critical value of the on-site repulsion term [9]).

We report here on our investigation of the electronic and magnetic properties of graphane and their modification once the H-vacancy defects are introduced in the lattice. Our study is performed via the quantum-chemistry methods using the spin-polarized density functional theory with the semilocal gradient corrected functional (UB3LYP/6-31G) in the Jaguar 7.5 program [21]. The H-vacancies are introduced in the originally optimized structure of defect-free graphane in the chair conformation (for the size of the graphane flake see Fig.), whose carbon atoms at the edges are terminated by two hydrogen atoms thereby preserving the sp^3 network over the whole lattice.

SINGLE H-VACANCY DEFECT

The size of the band gap of graphane nanoribbons decreases exponentially with increasing nanoribbon width as a result of vanishing of the confinement effect [12] similarly to that in graphene [13]. Therefore, for graphane flakes confined by the edges from all sides of size $10\text{\AA} \times 16\text{\AA}$ suggesting strong confinement effect, the large band gap in comparison to that obtained for nanoribbons [12, 15, 19] is expected. Defect-free graphane flakes

of size $10\text{\AA} \times 16\text{\AA}$ with edges possessing sp^3 hybridization are found to be characterized by degenerate bands and by a band gap of 7.51 eV (the highest and lowest molecular orbitals are HOMO=-6.09 eV and LUMO=1.42 eV, respectively), as shown in Fig. (a). For comparison we have examined flakes of size $18\text{\AA} \times 16\text{\AA}$ and found a decrease in gap to 7.15 eV (HOMO=-5.87 eV and LUMO=1.27 eV). The edges in the sp^2 hybridization, for which the edge carbon atoms are terminated by a single hydrogen, possess the localized states. In this case the orbital degeneracy is lifted and the gap decreases to 3.04 eV (HOMO=-4.64 eV and LUMO=-1.58 eV). In the available experiment [16, 17], only a transformation of graphene from the conductor to an insulator due to its hydrogenation was reported, but the size of the gap and the type of edge hybridization were not indicated. Since we found that the gap is sensitive to edge hybridization and can be increased from 3.04 eV to a maximum of 7.51 eV by its transformation from sp^2 to sp^3 type, this issue should be the top priority for further experimental investigations.

A single H-vacancy defect in the graphane lattice generates an unsaturated dangling bond on the carbon atom - π unpaired electron (perpendicular p_z orbital). Moreover, bonding of the carbon atom carrying the defect with its neighbors is changed from the sp^3 hybridization to sp^2 , thus providing a modification of the bond length from 1.55 Å to 1.52 Å. The perpendicular p_z orbital and the C-C bonds possessing sp^2 hybridization participate in the formation of the localized state characterized by an unpaired spin (see the spin density in Fig.). Therefore, this localized state is spin-polarized and generates a defect level in the band gap (see the bands in Fig. (b)). For the α -spin state, the defect level (π) appears close to the valence band (HOMO=-4.55 eV) thereby suppressing the size of the gap to $\Delta_\alpha=6.06$ eV, while for the β -spin state the π^* level occurs closer to the conduction band (LUMO=-0.84 eV) and the gap is $\Delta_\beta=5.29$ eV.

DIFFERENT DISTRIBUTION OF THE H-VACANCY DEFECTS

For several H-vacancy defects, ordering of spins of the localized states and the size of the bandgap are defined by the distance between the defects and the distribution of those defects between the sides of the graphane plane. The side dependence is related to the sublattice symmetry. For the chair conformation of graphane, the carbon atoms belonging to different sublattices are terminated by the hydrogen atoms from different sides of the plane. It was already known that in graphene [22], when the localized states occupy the same sublattice and if their spins have antiparallel alignment, then the contribution of the π states to the total energy diminishes as a result of the destructive interference between the spin-up and

spin-down tails. Therefore, according to Lieb's theorem [5] for the localized states occupying the same sublattice a ferromagnetic ordering of their spins would be energetically favored, but for the states on different sublattices, one expects the antiferromagnetic ordering [6-9].

For vacancies equally distributed between both sides of the graphane plane (AB -distribution), the energetically favorable spin ordering is the antiparallel alignment of spins between one side (A sublattice) and the other (B sublattice). Thus, for even number of vacancies in the AB -distribution, all spins are paired but the band degeneracy can be slightly lifted. In Fig. (c) we present the bands for two H-vacancy defects in the AB -distribution separated by a distance $d = 3a_{C-C}$, where a_{C-C} is the length of the C-C bond. Therefore for the α - and β -spin states, the obtained band gap of the size $\Delta_{\alpha,\beta} = 5.41$ eV is defined by the energy gap between the π (HOMO=-4.56 eV) and the π^* (LUMO=-0.85 eV) defect levels. For odd number of defects, one localized state would have unpaired spin which generates an extra level π for the α - and π^* for the β -spin states. However, when several H-vacancy defects are located on the same side of the graphane plane the parallel alignment of their spins would be preferred because they belong to the same sublattice (AA -distribution). In Fig. (d) we show the energetics of the bands for graphane with two H-vacancy defects separated by a distance of $d = 4a_{C-C}$ in its triplet state. Each spin state induces a defect level in the valence band of the α -spin state (π states) and in the conduction band of the β -spin state (π^* states). Therefore, the size of the bandgap for the α -state is defined by the conduction band and the defect level π in the valence band, while for the β -spin state by the valence band and the defect level π^* in the conduction band ($\Delta_\alpha=6.08$ eV, $\Delta_\beta=5.24$ eV) that is similar to the case of the single H-vacancy (see Fig. (b)). However, the state characterized by antiparallel alignment of two spins (the singlet state), possesses the π and π^* defect levels for both the α - and β -spin states and the size of the bandgap is defined by the energy gap between these defect levels, π and π^* , i.e., $\Delta_\alpha \simeq \Delta_\beta$ (for example see Fig. (c)).

The destructive and constructive contributions of the spin tails of the localized states decrease with increasing distance between the defects [22]. Therefore, we have calculated the difference in the total energy between the triplet and singlet states ($E_{(\frac{3}{2};\frac{1}{2})}$) depending on the distance between the two H-vacancy defects. If $E_{(\frac{3}{2};\frac{1}{2})}$ energy is negative the ferromagnetic ordering of spins is energetically preferred, but an antiferromagnetic ordering otherwise. We have calculated the two components: the energy $E_{(\frac{3}{2};\frac{1}{2})}^0$ is considered before relaxation of the lattice induced by the presence of defects and the $E_{(\frac{3}{2};\frac{1}{2})}$ component after relaxation. These energies for the AA - and AB -distributions and splitting of the π levels in the valence band ($\varepsilon_1 - \varepsilon_2$) are presented in Table I. For

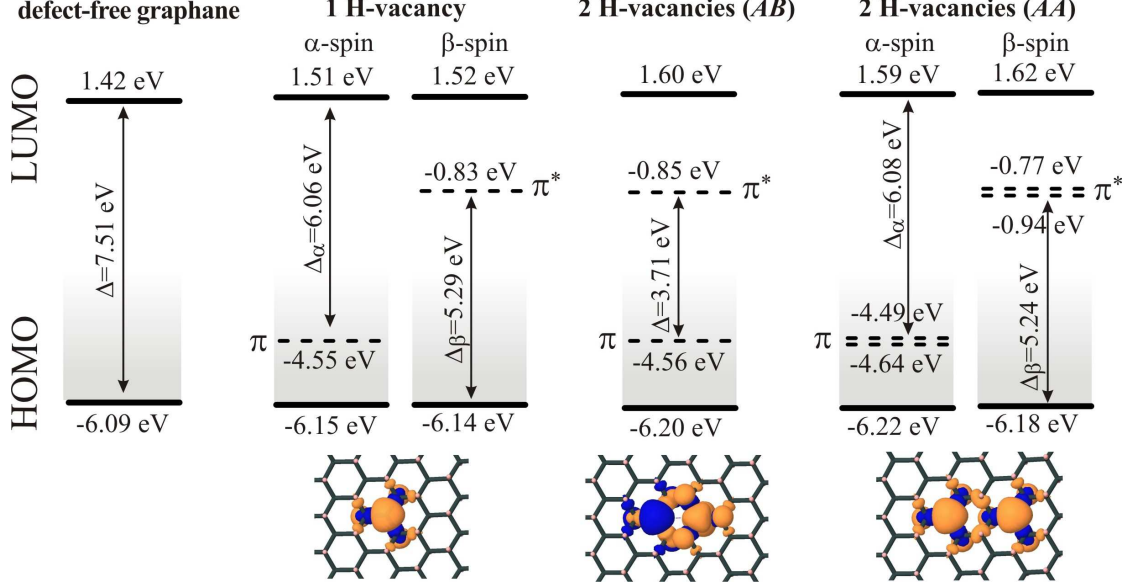


FIG. 2: Energetics of the bands in graphane with sp^3 hybridized edges (solid lines) and the defect levels (π and π^*) induced by H-vacancies (dashed lines): (a) defect-free graphane; (b) graphane containing a single H-vacancy; (c) graphane containing two H-vacancies distributed between the two sides of the graphane plane (AB -distribution) and separated by a distance of $d = 3a_{C-C}$ (antiferromagnetic spin ordering); (d) graphane containing two H-vacancies located on one side of the graphane plane (AA -distribution) and separated by the distance of $d = 4a_{C-C}$ (ferromagnetic spin ordering). The spin density plotted with isovalues of $\pm 0.001 \text{ e}/\text{\AA}^3$ is also presented.

the AB -distribution the distance between the two defects should be $> a_{C-C}$ because for $d = a_{C-C}$ the spins of the two localized states are paired which leads to transformation of a single bond in sp^3 hybridization between the nearest-neighbor carbon atoms to a double bond in sp^2 hybridization (σ and π bonds) of length 1.36 Å. Such a defect forms the π and π^* defect levels which are energetically close to the edges of the conduction and valence bands of graphane. Therefore, the size of the band gap defined by the defect levels is 6.38 eV, that is much larger than that for the levels formed by the non-bonded perpendicular p_z orbital ($\Delta = 3.71 \text{ eV}$ in Fig. (c)).

A significant energy difference between the triplet and the singlet states was found only for $d \leq 2a_{C-C}$ in the AA -distribution for which the relaxation of the graphane lattice stabilizes the state with ferromagnetic spin ordering, and for $d < 2a_{C-C}$ in the AB -distribution. As a result, for the nearest location of the defects, the ordering of spins is according to Lieb's theorem [5]. When the defects are spatially separated ($d > 2a_{C-C}$) the energy difference between the state with a large spin number and the singlet state diminishes because of decoupling of the magnetic moments of the localized states and the random spin distribution with a minimum number of unpaired spins would be energetically favored. Therefore, for even number of defects the system would prefer to remain in the singlet state independent of the distribution of defects over the sublattices, while for odd number of defects the triplet state is preferred.

TABLE I: Difference in the total energy between the triplet and singlet states for the non-optimized plane of graphane with two defects $E_{(\frac{3}{2}; \frac{1}{2})}^0$ and after its full relaxation $E_{(\frac{3}{2}; \frac{1}{2})}$. $(\varepsilon_1 - \varepsilon_2)$ is the energy splitting of the π orbitals for the relaxed lattice of graphane with two defects.

distance	$E_{(\frac{3}{2}; \frac{1}{2})}^0$ (eV)	$E_{(\frac{3}{2}; \frac{1}{2})}$ (eV)	$(\varepsilon_1 - \varepsilon_2)$ (eV)
AA-distribution (ferromagnetic ordering)			
$d = 2a_{C-C}$	-1.52	-1.23	2.82×10^{-1}
$d = 4a_{C-C}$	-0.26	-1.32×10^{-2}	1.52×10^{-1}
$d = 6a_{C-C}$	7.11×10^{-5}	-1.15×10^{-2}	1.53×10^{-2}
$d = 8a_{C-C}$	1.76×10^{-5}	-7.93×10^{-3}	6.52×10^{-3}
AB-distribution (antiferromagnetic ordering)			
$d = a_{C-C}$	1.34	2.98	-
$d = 3a_{C-C}$	4.30×10^{-3}	1.18×10^{-2}	-
$d = 5a_{C-C}$	-1.08×10^{-4}	6.13×10^{-3}	-

We have calculated the fluctuation of the gap size with increasing number of defects for the system in its singlet state when the size of the gap is defined by the energy difference between the induced defect levels, π and π^* , formed by the perpendicular p_z orbitals. For the AB -distribution ($d > a_{C-C}$), the size of the gap can fluctuate from 1.2 to 3.7 eV depending on the distance between the defects and their locations. The change in the gap size is related to the degree of the broken sublattice sym-

metry. Moreover, with increasing concentration of the H-vacancies ($N > 8$) we found that the number of localized states can be smaller than the number of defects. For the *AA*-distribution the size of the gap is found to gradually decrease from 3.75 to 2.72 eV with increasing number of defects from $N = 2$ to $N = 18$. Additionally, with a growing number of defects a significant distortion of the planarity of graphane, such as buckling of the lattice inherent for the *AA*-distribution, was observed.

STABLE FERROMAGNETISM

A prediction of the ordering of the *AA*-distributed localized states on the graphane surface is controversial. According to results in [24] for semihydrogenated graphene, i.e. graphene hydrogenated from one side (the so called graphone), the non-hydrogenated side of graphane is possessing the localized states and the spins all of them are ferromagnetically ordered. We believe that this behavior is highly debatable because it is known for the carbon-like materials, such as diamond and graphitic structures, that the total magnetization is suppressed by increasing the vacancy concentrations, and particularly for graphitic structures this occurs more rapidly [10]. In contrast, authors of Ref. [20] did not consider the ferromagnetic ordering of the states in defected graphane at all because they found that for the vacancy defects located on the neighbors ($d = 2a_{C-C}$), the spins are paired, indicating a nonmagnetic state. When the distance exceeds $2a_{C-C}$ for which pairing of the spins can not occur, the interaction between the localized states vanish, thereby favoring the antiferromagnetic ordering of spins. However, we believe that pairing of the spins of the localized states located on the neighboring carbon atoms is unlikely, considering the significant distance between the vacancies (~ 2.55 Å). Moreover, pairing may occur only when the spins are antiferromagnetically ordered (that for the states localized on the same sublattice is against the Lieb's theorem [5]) and it implies the formation of the bond, which again seems unlikely because of the large distance between the localized states (the typical *C*–*C* bond length in organic compounds is ~ 1.4 Å against ~ 2.55 Å for the states separated by $d = 2a_{C-C}$ in graphane). Therefore, the question of ordering of spins of the localized states in their *AA* distribution is unclear as yet which we set out to investigate here.

We found that for the *AA*-distribution of the localized states formed by the H-vacancies, the ferromagnetic ordering of their spins is possible when the vacancies are placed on the neighboring carbon atoms (see $E_{(\frac{8}{2};\frac{1}{2})}^0$ for the *AA*-distribution in Table I), thereby generating a state characterized by a large spin number (see an example for graphene in Ref. [23]). Just as in [20] it was noticed that increasing the distance between the vacancies leads to vanishing of π - π interaction between local-

ized states resulting in the antiferromagnetic ordering of spins. Therefore, we investigating here the stability of the ferromagnetic ordering of the spins of the localized states placed on the neighboring carbon atoms ($d = 2a_{C-C}$) and formation of domains of defects depending on the concentration of the defects in domain and number of domains.

We found that with increasing concentration of defects (N) the stability of the state with a large spin number, i.e., the difference in total energy between the state with a large spin number and the singlet states, can increase. Therefore, for two parallel lines of defects $E_{(\frac{4}{2};\frac{1}{2})}^0 = -3.32$ eV for $N = 4$ (Fig. (a) for the spin density distribution of $N = 4$), $E_{(\frac{6}{2};\frac{1}{2})}^0 = -5.03$ eV for $N = 6$ and $E_{(\frac{8}{2};\frac{1}{2})}^0 = -6.56$ eV for $N = 8$. However, for $N = 8$ the states characterized by the lower spin number are close in energy to the state with the larger spin number ($E_{(\frac{8}{2};\frac{6}{2})}^0 = -0.035$ eV, $E_{(\frac{8}{2};\frac{4}{2})}^0 = -0.065$ eV and $E_{(\frac{8}{2};\frac{2}{2})}^0 = -0.12$ eV) thereby destabilizing it and limiting the number of defects having ferromagnetically ordered spins. A further increase of the defect concentration ($N > 8$) leads to significant suppression of the energy difference between the ferromagnetic and singlet states. Thus, $E_{(\frac{10}{2};\frac{1}{2})}^0 = -0.25$ eV for $N = 10$, $E_{(\frac{12}{2};\frac{1}{2})}^0 = -0.17$ eV for $N = 12$ and $E_{(\frac{14}{2};\frac{1}{2})}^0 = -0.14$ eV for $N = 14$. Therefore, just as for graphene [6–9], there is a critical value of defect concentration above which the ferromagnetic ordering of the spins of the localized states occupying the same sublattice no longer exists. Another destabilizing factor for ferromagnetism in graphane containing many H-vacancies in the *AA*-distribution is the lattice relaxation leading to the buckling of the graphane structure ($E_{(\frac{4}{2};\frac{1}{2})}^0 = -1.49$ eV for $N = 4$ and $E_{(\frac{8}{2};\frac{1}{2})}^0 = 1.29$ eV for $N = 8$). There is also a significant decrease in stability when the defects are divided in groups, because the state characterized by antiferromagnetic ordering of spins between the groups is close in energy to that of the state with ferromagnetic ordering of all spins (see the spin density distribution for $N = 4$ in Fig. (b)). Finally, since graphane is a wide gap semiconductor and possess no localized states at the edges which could interact (π – π interaction) with states formed by the H-vacancy defects, the increasing size of the graphane flakes leading to suppression of the graphane gap should not drastically alter the interaction of the localized states and their ordering, which was the case in graphene [8].

To summarize, for the *AA*-distribution of the H-vacancies the size of the band gap can be tuned by the level of hydrogenation – the gap slowly decreases with increasing number of defects, while for the *AB*-distribution the size of the gap fluctuates in the range of 1.2 – 3.7 eV depending on the level of the broken sublattice symmetry. Moreover, formation of the H-vacancy defects redistributed over one side of the graphane plane

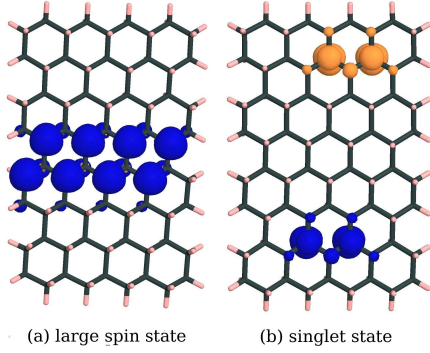


FIG. 3: Spin density for the AA-distribution of H-vacancies (a) 8 H-vacancies ($E_{(\frac{8}{2}; \frac{1}{2})}^0 = -6.36$ eV), (b) 4 H-vacancies in the singlet state ($E_{(\frac{4}{2}; \frac{1}{2})}^0 = 4.81 \times 10^{-5}$ eV). Spin densities are plotted with isovalues of ± 0.005 e/ \AA^3 .

(AA-distribution) and located on the neighboring carbon atoms belonging to the same sublattice will generate a stable state characterized by a large spin number (ferromagnetic ordering). For a better stabilization of this state, the reorganization of the graphane lattice in response to the occurrence of defects should be minimized. Deformation of the graphane lattice can be minimized for free standing graphane in the low-temperature regime and through interaction of graphane with a substrate under the condition that the sp^3 hybridization of graphane lattice is preserved. If the rigidity of graphane on a substrate could be achieved, graphane containing H-vacancies on one side of the plane can even become a room-temperature ferromagnet, that obviously has enormous potentials for application in nanoelectronics and spintronics. Because each defect forms a perpendicular p_z orbital possessing unpaired spin and, therefore, its contribution to the magnetization is $1\mu_B$, the magnitude of magnetization of such room temperature ferromagnet can ideally be regulated by the number of H-vacancy defects. However, the number of defects to achieve the stable ferromagnetism at room temperature should be limited because above a critical value the ferromagnetic ordering of spins would be unstable.

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